

1 Stratospheric Observations of **CH₃D** and **HDO** from **ATMOS** infrared Solar Spectra:
2 **Enrichments of deuterium** in methane and implications for **IID**.
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18 Abstract

19 Stratospheric mixing ratios of CH₃D from 100 mb to 17mb (≈ 15 to 28 km) and HDO from 100 mb
20 to 10 mb (≈ 15 to 32 km) have been inferred from high resolution solar occultation infrared spectra
21 from the Atmospheric Trace MOlecule Spectroscopy (ATMOS) Fourier-transform interferometer.
22 The spectra, taken on board the Space Shuttle during the Spacelab 3 and ATLAS-1, -2, and -3
23 missions, extend in latitude from 70°S to 65°N. We find CH₃D entering the stratosphere at an
24 average mixing ratio of $(9.9 \pm 0.8) \times 10^{-10}$ with a D/H ratio in methane $(7.1 \pm 7.4)\%$ less than that in
25 Standard Mean Ocean Water (SMOW) (1σ combined precision and systematic error). In the mid to
26 lower stratosphere, the average lifetime of CH₃D is found to be (1.19 ± 0.02) times that of CH₄,
27 resulting in an increasing D/H ratio in methane as air “ages” and the methane mixing ratio
28 decreases. We find an average of (1.0 ± 0.1) molecules of stratospheric HDO are produced for each
29 CH₃D destroyed (1σ combined precision and systematic error), indicating that the rate of HDO
30 production is approximately equal to the rate of CH₃D destruction. Assuming negligible amounts
31 of deuterium in species other than HDO, CH₃D and HD, this limits the possible change in the
32 stratospheric HD mixing ratio below about 10mb to be ± 0.1 molecules HD created per molecule
33 CH₃D destroyed,

1 Introduction

2 In the stratosphere, H_2O is created primarily by oxidation of CH_4 and H_2 by OH, Cl and
3 O(1D). Likewise, oxidation of CH_3D and HD creates HDO, but these deuterated species show a
4 sufficiently different reactivity with surrounding chemical species so that their measurement can
5 provide additional insight into the stratospheric hydrogen budget. In understanding the deuterium
6 budget of the stratosphere, and relating it to the hydrogen budget, two questions arise. First, what
7 is the lifetime of CH_3D compared to that of CH_4 , or put another way, how does the D/H ratio in
8 methane vary with the CH_4 mixing ratio? Second, is the rate of stratospheric HDO production
9 balanced by that of CH_3D oxidation? If not, could there be a net production or destruction of HD,
10 and possibly a change in the D/H ratio of molecular hydrogen, due to a difference in the rates
11 between CH_3D oxidation to HD and HD oxidation to HDO? (Discussion of the D/H ratio in
12 stratospheric water is in an accompanying paper by Moyer *et al.* [this issue].)

13 We address these questions using spectroscopic measurements of stratospheric CH_3D and
14 HDO mixing ratios using data from the ATMOS instrument. The ATMOS instrument, described in
15 detail by Farmer *et al.* [1987], is a Fourier-transform infrared (FTIR) interferometer that gathered
16 spectral absorption measurements at a resolution of 0.01 cm^{-1} from solar occultations on board
17 four Space Shuttle missions (see Gunson *et al.* [this issue]). A previous report of HDO and CH_3D
18 results from ATMOS was made by Rinsland *et al.* [1991] with data from the Spacelab 3 mission;
19 however, their report did not relate changes in the CH_3D mixing ratio to those in HDO. With the
20 combined Spacelab 3 and ATLAS-I, -2, and -3 missions, a much broader latitudinal coverage and
21 many more vertical mixing ratio profiles were obtained, allowing characterization of the CH_3D and
22 HDO budget on a more global basis. An important addition to previous reports is measurement of
23 CH_3D inside the Arctic and Antarctic vortices. Above 28 km, the molecular density of CH_3D is
24 normally too low to gain an adequate spectral absorption signal with the ATMOS instrument.

However, the descent of upper stratospheric air to altitudes below 28 km inside the vortices [Abrams *et al.*, this issue a,b] allows measurement of CH₃D in “old” air that would be otherwise impossible to measure. As stratospheric dehydration is not the focus of this letter, we do not report measurements of HDO inside the polar vortices. Analyses are cent *inuing* on these vortex HDO measurements, and they will be the focus of an upcoming paper.

In this paper, the delta notation is used to describe isotopic fractionation as the difference in parts per thousand of an isotopically labelled species with respect to a standard, c. g.,

$$\delta D_{\text{sample}} (\text{‰}) = 1000 \times \frac{(D/H)_{\text{sample}} - (D/H)_{\text{standard}}}{(D/H)_{\text{standard}}} \quad (1)$$

Standard Mean Ocean Water (SMOW) is used for the standard D/H ratio (see IUPAC [1983]) and we use the recommended value of $(155.76 \pm 0.05) \times 10^{-6}$ [Hagemann *et al.*, 1970].

Observations and data analysis

information about ATMOS on the shuttle missions, and discussion of the mixing ratio retrieval process, can be found in Gunson *et al.* [this issue]. For the results described here, spectral lines of the ν_2 band of HDO and the ν_1 band of Cl I₃D were analyzed, and spectral intervals used for these analyses are described in Table 1. HDO is best observed in filters 2 (1100-2000 cm⁻¹) and 9 (600-2450 cm⁻¹), while CH₃D could only be observed in filter 3 (1580 - 3400 cm⁻¹). However, CH₄ can be analyzed in all of these filters and, with a correlation of CH₃D to CH₄ in filter 3, we are able to infer the mixing ratio of CH₃D in filters 2 and 9 from CH₄ mixing ratios. At polar latitudes, determination as to whether a Cl I₃D measurement was inside or outside the vortex was based on visual inspection of co-located mixing ratio profiles of CH₄ and N₂O, as these gases show markedly smaller mixing ratios inside the vortex than outside at similar altitudes (see Abram *et al.* [this issue a,b]). “Vortex edge” observations were not used. CH₃D results are presented from tangent pressures of 100mb to 17mb, and HDO results are from 100mb to 10mb.

Before final analyses, data were filtered by rejecting any observations with an estimated random error greater than 30% for CH₃D and HDO, or 10 % for Cl I₄. This step eliminated about 16% of the filter 3 CH₃D data and about 19% of the filter 2 and 9 HDO data. Systematic biases, mostly from errors in line intensities, are estimated to be 7% for CH₃D, 6% for HDO, and 5% for CH₄ (see *Gunson et al.* [this issue]).

CH₃D measurement and the D/H ratio in methane

Rate constants for reactions of OH or Cl with CH₃D are lower than those for CH₄ [*DeMore et al.*, 1994; *Wellington and Hurley*, 1992], but any isotope effect between the rate constants of the excited O(¹D) + CH₃D and that of O(¹D) + CH₄ is expected to be relatively minor [*Kaye*, 1987]. To estimate these combined effects on the D/H ratio of methane, we begin by assuming that in the mid to lower stratosphere CH₄ and CH₃D are only destroyed by OH, Cl, and O(¹D) oxidation, and photolysis is negligible. The oxidation of CH₃D and CH₄ can then be described by:

$$\frac{1}{[\text{CH}_3\text{D}]} \frac{d[\text{CH}_3\text{D}]}{dt} = -k_{\text{OH}}^*[\text{OH}] - k_{\text{Cl}}^*[\text{Cl}] - k_{\text{O}^1\text{D}}^*[\text{O}^1\text{D}] \quad (2)$$

$$\frac{1}{[\text{CH}_4]} \frac{d[\text{CH}_4]}{dt} = -k_{\text{OH}}[\text{OH}] - k_{\text{Cl}}[\text{Cl}] - k_{\text{O}^1\text{D}}[\text{O}^1\text{D}] \quad (3)$$

Let $\gamma_i(T)$ equal the ratios of the rate constants. That is, $\gamma_{\text{OH}}(T) = k_{\text{OH}}^*/k_{\text{OH}}$, $\gamma_{\text{Cl}}(T) = k_{\text{Cl}}^*/k_{\text{Cl}}$, and

$\gamma_{\text{O}^1\text{D}}(T) = k_{\text{O}^1\text{D}}^*/k_{\text{O}^1\text{D}}$, where T is temperature. Subtraction of Equation (3) from (2) gives:

$$\frac{1}{[\text{CH}_3\text{D}]} \frac{d[\text{CH}_3\text{D}]}{dt} - \frac{1}{[\text{CH}_4]} \frac{d[\text{CH}_4]}{dt} = -(\gamma_{\text{OH}} - 1)k_{\text{OH}}[\text{OH}] - (\gamma_{\text{Cl}} - 1)k_{\text{Cl}}[\text{Cl}] - (\gamma_{\text{O}^1\text{D}} - 1)k_{\text{O}^1\text{D}}[\text{O}^1\text{D}] \quad (4)$$

But we note that

$$k_{OH}[OH] = \frac{1}{[CH_4]} \frac{d[CH_4]}{dt} f_{OH}(z) \quad (5)$$

where $f_{OH}(z)$ is the fraction of all CH_4 destroyed at altitude z that is destroyed by OH. Similar definitions for $f_{Cl}(z)$ and $f_{O(^1D)}(z)$, substitution in (4) for k_{OH} , k_{Cl} , and $k_{O(^1D)}$ (noting that they sum to unity), and rearrangement yield:

$$\frac{1}{[CH_3D]} \frac{d[CH_3D]}{dt} = (\gamma_{OH} f_{OH} + \gamma_{Cl} f_{Cl} + \gamma_{O(^1D)} f_{O(^1D)}) \frac{1}{[CH_4]} \frac{d[CH_4]}{dt} \quad (6)$$

or:

$$\frac{1}{[CH_3D]} \frac{d[CH_3D]}{dt} = \kappa(T,z) \frac{1}{[CH_4]} \frac{d[CH_4]}{dt} \quad (7)$$

where $\kappa(T,z)$ is the term inside the parentheses of (6). Note that the left hand side of Equation (7) is the time constant for destruction of CH_3D , or equivalently, its inverse lifetime. Thus, for a $\kappa(T,z) < 1$, the lifetime of CH_3D is longer than that of CH_4 . We estimate an "average" κ in the mid to lower stratosphere by assuming average fractions for destruction (i.e., f_{OH} , f_{Cl} , and $f_{O(^1D)}$), and assuming that the ratios of the rate constants, γ , are constant with the temperature range in the mid to lower stratosphere and that mixing effects are minor. Integrating (6), assigning boundary conditions, and dividing by total molecular concentration to get mixing ratios (χ) yield:

$$\ln \chi(CH_3D) = \ln \chi_0(CH_3D) + \kappa_{av} \ln \frac{\chi(CH_4)}{\chi_0(CH_4)} \quad (8)$$

or equivalently,

$$\frac{\chi(\text{CH}_3\text{D})}{\chi_0(\text{CH}_3\text{D})} = \left(\frac{\chi(\text{CH}_4)}{\chi_0(\text{CH}_4)} \right)^{\kappa_{\text{av}}} \quad (9)$$

where $\chi_0(\text{CH}_3\text{D})$ and $\chi_0(\text{CH}_4)$ are the initial mixing ratios of these gases as they enter the stratosphere. A rough estimate of κ_{av} can be made if we set $\gamma_{\text{OH}}=0.67$ (averaged from 190K to 250K using the rate constants reported by *DeMore et al. [1994]*), $\gamma_{\text{Cl}}=0.735$ (from the evaluation by *Wallington and Hurley [1992]* at 295 K), and $\gamma_{\text{O}(^1\text{D})}\approx 1$ (see *Kaye [1987]*). Model calculations by one of us (RJS) indicate that between about 16 km and 30 km, about 50% of the destruction of CH_4 is by OH, 29% by Cl and 21 % by $\text{O}(^1\text{D})$. Substituting these laboratory data and model results, $\kappa_{\text{av}}\approx 0.78$, suggesting that the lifetime of CH_3D is significantly longer than that of CH_4 , and enrichment of deuterium in methane can occur as the CH_4 mixing ratio decreases. We emphasize that this is only a rough estimation as none of the experiments measuring the kinetic rate constants of OH or Cl with CH_3D were made at the cold temperatures typical of the lower stratosphere, and we are unaware of any laboratory measurements of the $\text{O}(^1\text{D}) + \text{CH}_3\text{D}$ rate constant.

ATMOS measurements of the mixing ratios of CH_3D are plotted against co-located measurements of CH_4 in the upper panel of Figure 1. We assume that $\chi_0(\text{CH}_4) = (1.71 \pm 0.03) \times 10^{-6}$ (from global 1992 tropospheric measurements reported in *WMO [1995]*, and where we have assumed a 2% error). From a best fit line of $\ln \chi(\text{CH}_3\text{D})$ vs $\ln \chi(\text{CH}_4)$, we observe $\kappa_{\text{av}} = (0.84 \pm 0.02)$ (1 σ combined precision and systematic error), higher than our initial estimate of 0.78. Note that the error in κ_{av} is not affected by systematic errors in the measured

stratospheric mixing ratios of CH_3D and CH_4 (which instead affect the error in the intercept). On average, the stratospheric lifetime of CH_3D should be κ_{av}^{-1} ($=1.19 \pm 0.02$) times that of CH_4 , or about 190 years based on a stratospheric CH_4 lifetime of 160 years [Prather and Spivakovsky, 1990]. From the fitted line at a tropospheric CH_4 mixing ratio of $(1.71 \pm 0.03) \times 10^{-6}$, we find the mixing ratio of CH_3D entering the stratosphere to be $(9.9 \pm 0.8) \times 10^{-10}$ (1 σ combined precision and systematic error).

The lower panel of Figure 1 shows the enrichment of CH_3D with CH_4 mixing ratio, as well as the average enrichment calculated using the fitted line from the upper panel. Although there is considerable scatter in the data, it is seen that methane becomes progressively enriched in deuterium as the mixing ratio of CH_3D decreases. With a tropospheric CH_4 mixing ratio of $(1.71 \pm 0.03) \times 10^{-6}$, the average δD in methane entering the stratosphere is $-(7.1 \pm 7.4)\text{‰}$ (1 σ combined precision and systematic error). This is within error of the ATMOS Spacelab 3 measurements of Rinsland *et al.* [1991], who found δD in stratospheric methane near latitudes of 30°N and 49°S to be $-(49 \pm 44)\text{‰}$ and $+(24 \pm 125)\text{‰}$ respectively. This is also within error of free tropospheric measurements by Ehhalt [1973], who reported values of -86‰ and -94‰ , and Wahlen *et al.* [1987], who reported $-(80 \pm 8)\text{‰}$.

Measurement of HDO vs CH_3D and implications for HD

In the mid to lower stratosphere, atomic H is distributed primarily among CH_4 , H_2O and H_2 , with negligible amounts among other species. It appears that oxidation of H_2 is roughly balanced by its production via oxidation of CH_4 through a short-lived C_2H_2 intermediate [Dessler *et al.*, 1994; Abbas *et al.*, this issue]. Similarly, deuterium is most likely distributed mainly among CH_3D , HDO, and HD (with HD produced by oxidation of CH_3D and destroyed by oxidation to HDO). However, in the mid to lower stratosphere, it may not necessarily be the case that the

1 mixing ratio of HD is as weakly varying as that of H₂. As suggested by *Ehhalt et al. [1989]*, the
 2 lower reaction rate constant of OH and HD compared to that of OH and H₂ may serve to enrich
 3 tropospheric hydrogen gas in deuterium. However, stratospheric destruction of HD is regulated
 4 not only by rates of OH attack, but also to a large extent by those of O(¹D), and the rate constant of
 5 the O(¹D) reaction is not expected to be significantly affected by deuterium substitution [*Kaye*,
 6 1987]. (Reaction with Cl is a much more minor sink for hydrogen than for methane using the rate
 7 constants given by *DeMore et al. [1994]*.) For production of HD, account must be taken of not
 8 only the oxidation rates of CH₃D, but also the partitioning of D in the short-lived species in the
 9 reaction pathway from CH₃D to HD (e.g. the yield of CH₂D vs CH₃, or that of CHDO vs CH₂O).
 10 In the absence of direct measurement of HD, a test for changes in the HD mixing ratio is examina-
 11 tion of those for HDO and CH₃D. Assuming the sum of the mixing ratios of HDO, CH₃D, and
 12 HD constant, then:

$$\frac{d\chi(\text{HDO})}{d\chi(\text{CH}_3\text{D})} + \frac{d\chi(\text{HD})}{d\chi(\text{CH}_3\text{D})} = -1 \quad (10)$$

14 and any deviation of $d\chi(\text{HDO})/d\chi(\text{CH}_3\text{D})$ from -1 through the mid and lower stratosphere implies
 15 a changing mixing ratio of HD.

16 In order to compare HDO and CH₃D mixing ratios, we use the relationship in Equation 8
 17 (with $\kappa=0.84\pm0.02$, $\chi_0(\text{CH}_4) = (1.71\pm0.03)\times10^{-6}$, and $\chi_0(\text{CH}_3\text{D})=(9.9\pm0.8)\times10^{-10}$) to estimate
 18 the CH₃D mixing ratio in filters 2 and 9 from measurements of CH₄. Figure 2 is a scatter plot of
 19 the HDO mixing ratio versus this derived CH₃D mixing ratio. We calculate $d\chi(\text{HDO})/d\chi(\text{CH}_3\text{D})$
 20 by a least-squares straight line fit, but fitted only where CH₄ mixing ratios were less than 1.4×10^{-6}
 21 to avoid seasonal effects in HDO in the lower stratosphere. The calculated slope, $-(1.0\pm0.1)$ (1 σ
 22 combined precision and systematic error), indicates that HDO production is in near balance with

CH₃D destruction. Large effects are still possible for HD within the error, however, As about 10% of stratospheric deuterium is in HD, small deviations in $d\chi(\text{HDO})/d\chi(\text{CH}_3\text{D})$ from -1 can have significant effects in the HD mixing ratio, similar to the case for H₂ (e.g. *Dessler et al. [1994]*). Large effects may also occur in the D/H ratio of stratospheric hydrogen, particularly if the H₂ mixing ratio does not change in the mid to lower stratosphere, While we cannot find statistically significant evidence for changes in H₂, the results in this report can provide some constraints below about 10 mb. To illustrate this, we assume a constant H₂ mixing ratio of 0.5×10^{-6} and a δD in hydrogen entering the stratosphere of $+(70 \pm 30)\text{‰}$ [*Friedman and Scholz, 1974*], giving an initial HD mixing ratio of $(1.67 \pm 0.05) \times 10^{-10}$. Results here indicate that if CH₃D enters the stratosphere at a mixing ratio of 9.9×10^{-10} , then when half of the CH₃D is destroyed, the change in the HD mixing ratio is constrained to be $\pm 5 \times 10^{-11}$ and the change in δD in hydrogen can be constrained to $\pm 320\text{‰}$.

Conclusions

We have analyzed ATMOS spectra for mid to lower stratospheric HDO and CH₃D mixing ratios. The average D/H ratio in methane entering the stratosphere was found to be $-(71 \pm 74)\text{‰}$, but as the lifetime for CH₃D is greater than that of CH₄ by a factor of (1.19 ± 0.02) , this D/H ratio increases as methane becomes oxidized. Stratospheric production of HDO is (1.0 ± 0.1) times that of CH₃D loss, and assuming deuterated species other than HDO, CH₃D and HD are in negligible abundance, changes in HD abundance are thus constrained to be ± 0.1 molecules HD per molecule CH₃D destroyed (1σ combined precision and systematic error). To better understand these phenomena, research is warranted into the partitioning of deuterium in CH₃D destruction products (including a comparison of the photolysis rates of CHDO vs that of CH₂O), and direct stratospheric measurements of the HD mixing ratio.

Acknowledgements

We thank L. R. Brown, T. L. Brown, J. C. Foster, C. B. Farmer, G. D. Lynch, O. F. Raper, and G. C. Toon for their assistance. Research was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract to the National Aeronautics and Space Administration.

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Table 1: Spectral intervals and lines used for HDO and CH₃D analyses

| Spectral interval Center (cm ⁻¹) | Interval Width (cm ⁻¹) | Altitude Range (km) | Line Center (cm ⁻¹) | Line Intensity at 296 K (cm molecule ⁻¹) | Air- broadened half-width (cm ⁻¹ /atm at 296K) | Ground- state energy (cm ⁻¹) | Temperature Sensitivity of Line Intensity at 230K (% K ⁻¹) |
|---|--|---------------------------|---------------------------------------|--|--|---|---|
| CH₃D | | | | | | | |
| 2950.84 | 0.24 | 10-28 | 2950.8514 | 2.81x10 ⁻²³ | 0.072 | 266.3 | 0.07 |
| 3061.56 | 0.20 | 15-36 | 3061.4148 | 5.21x10 ⁻²³ | 0.077 | 89.9 | -0.4 |
| 3078.34 | 0.17 | 15-28 | 3078.3125 | 1.61x10 ⁻²³ | 0.070 | 217.1 | -0.07 |
| | | | 3078.3551 | 2.09x10 ⁻²³ | 0.072 | 184.7 | -0.2 |
| 3098.91 | 0.15 | 10-24 | 3098.8832 | 1.58x10 ⁻²³ | 0.068 | 346.0 | 0.3 |
| HDO | | | | | | | |
| 1408.35 | 0.25 | 10-34 | 1408.3914 | 9.62x10 ⁻²⁴ | 0.102 | 29.8 | -0.6 |
| 1421.62 | 0.40 | 13-42 | 1421.6073 | 1.26x10 ⁻²³ | 0.077 | 233.1 | 0.02 |
| 1439.93 | 0.32 | 15-40 | 1439.8887 | 1.54x10 ⁻²³ | 0.095 | 150.1 | -0.2 |
| 1451.40 | 0.34 | 10-29 | 1451.4597 | 1.21x10 ⁻²³ | 0.093 | 265.2 | 0.07 |
| 1469.43 | 0.23 | 17-40 | 1469.3658 | 2.53x10 ⁻²³ | 0.095 | 156.4 | -0.2 |
| 1474.09 | 0.31 | 19-40 | 1474.1110 | 1.30x10 ⁻²³ | 0.094 | 156.4 | -0.2 |
| 1475.62 | 0.31 | 20-33 | 1475.5917 | 1.37x10 ⁻²³ | 0.096 | 150.2 | -0.2 |
| 1479.96 | 0.42 | 10-26 | 1480.0941 | 5.81x10 ⁻²⁴ | 0.093 | 225.9 | -0.04 |
| 1484.11 | 0.25 | 15-40 | 1484.1065 | 2.44x10 ⁻²³ | 0.092 | 225.9 | -0.04 |
| 1488.16 | 0.48 | 20-40 | 1488.0252 | 1.09x10 ⁻²³ | 0.093 | 221.9 | -0.04 |
| | | | 1488.1937 | 1.33x10 ⁻²³ | 0.100 | 32.5 | -0.6 |
| 1494.86 | 0.29 | 15-29 | 1494.8598 | 8.34x10 ⁻²⁴ | 0.095 | 221.8 | -0.05 |
| 1497.85 | 0.34 | 15-40 | 1497.8807 | 2.08x10 ⁻²³ | 0.085 | 308.6 | 0.02 |

Note: The temperature dependence for air-broadened half-widths is $T^{-0.75}$ for CH₃D and $T^{-0.64}$ for HDO. Line parameters for CH₃D are from *Rinsland et al. [1991]*. HDO line parameters are discussed in *Brown et al. [1995]*.

Figure captions

Figure 1: CH_3D mixing ratio vs CH_4 mixing ratio (upper panel) and δD in methane vs CH_4 mixing ratio (lower panel). Numbers in parentheses indicate the number of observations used: Spacelab 3: \boxtimes 48°S (9), \times 26°N-31°N (30); ATLAS-1: + 50 °S-200S (94); ATLAS-2: ∇ 50 °S-25°S (28), \sphericalangle 65 °N-700N outside vortex (21), ∞ 65 °N- 70°N inside vortex (63); ATLAS-3: \times 75°S-65°S outside vortex (86), $\#$ 75°S-65°S inside vortex (86), \square 0°-15°N (22), \diamond 15 °N-30°N (58), \bowtie 30°N-50°N (216). Note: Some polar profiles had regions inside and some regions outside the vortex.

Figure 2: HDO mixing ratio vs 1.1_3D mixing ratio. The line in the upper panel is fitted only where the CH_4 mixing ratio is less than 1.4×10^6 . Numbers in parentheses indicate the number of observations used: Spacelab 3: \boxtimes 49°S (13), \times 26 °N-31°N (33); ATLAS-1: + 55 °S-300S (118), \otimes 10°S-15°N (36), Δ 15°N-30°N (10); ATLAS-2: ∇ 50 °S-300S (40), \sphericalangle 65°N-70°N, outside vortex (35); ATLAS-3: \times 75°S-65°S, outside vortex (82), \square 12°N (4), \circ 15°N-30°N (25), \bowtie 30°N-50°N (12.2).

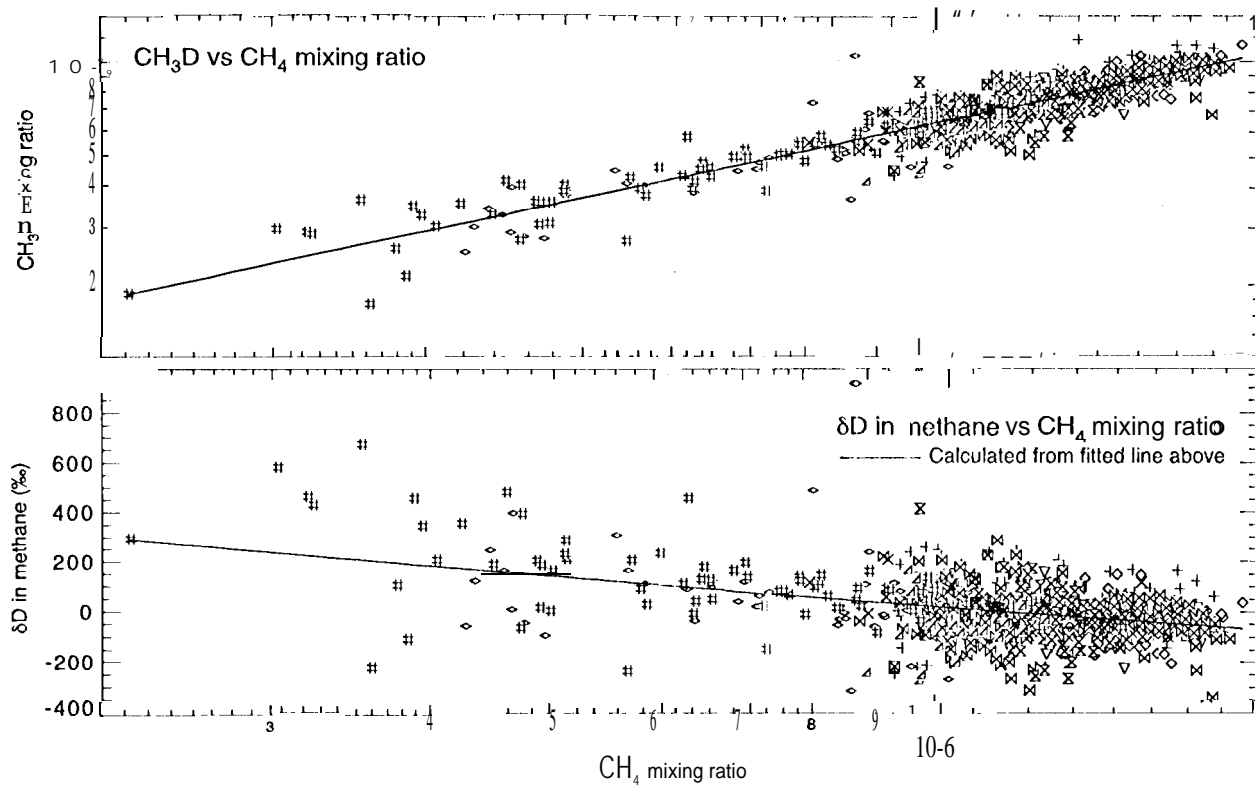


Figure 1

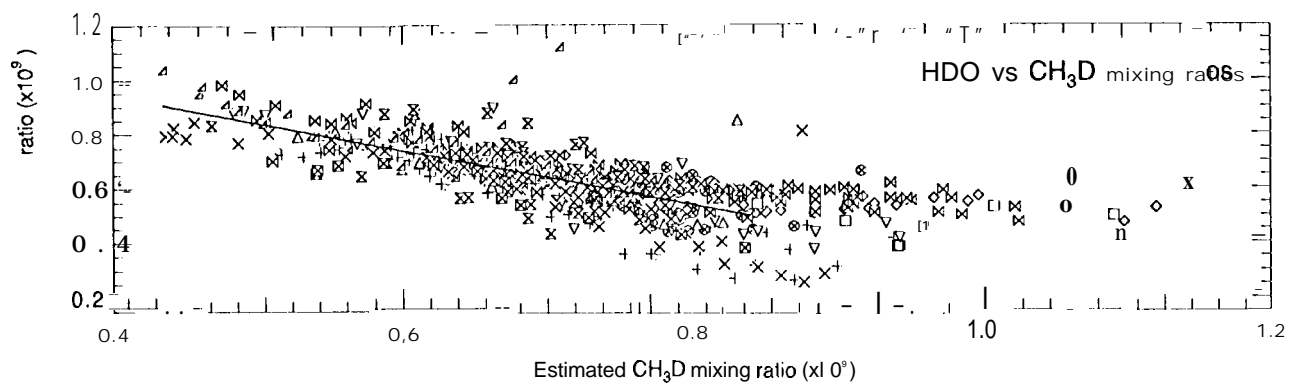


Figure 2